

Second-order post-Hartree-Fock perturbation theory for the electron current

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Based on the super-fermion representation of quantum kinetic equations we develop nonequilibrium, post-Hartree-Fock many-body perturbation theory for the current through a region of interacting electrons. We apply the theory to out of equilibrium Anderson model and discuss practical implementation of the approach. Our calculations show that nonequilibrium electronic correlations may produce significant quantitative and qualitative corrections to mean-field electronic transport properties. We find that the nonequilibrium leads to enhancement of electronic correlations.

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I. INTRODUCTION

The second order Møller-Plesset perturbation theory (MP2) is a very powerful tool for practical quantum chemical calculation.¹ MP2 accounts in many cases for the large fraction of post-Hartree-Fock electronic correlations. It gives quite accurate results for intermolecular interactions, molecular geometries, dissociation energies.¹ In this paper, we propose the extension of the MP2 theory to nonequilibrium, namely, we develop the second order post-Hartree-Fock perturbation theory for the electron current through a region of out of equilibrium, interacting electrons. As an example, we consider electron transport through Anderson model, but all our derivations are also directly applicable and transferable to a general molecular system connected to two metal electrodes and described by full many-electron Hamiltonian.

Recently, there have been several attempts to include post-Hartree-Fock electronic correlation into transport calculations through molecules.²⁻⁷ These approaches are mostly based on various implementation of nonequilibrium Green's function based GW theory. Our method is quite different. We start with kinetic equations for many-body density matrix. We convert the kinetic equation to the super-Fock space, separate Hartree-Fock and the normal ordered parts of the many-particle Liouvilian, and then develop nonequilibrium many body perturbation theory much along the lines of the traditional MP2 theory.

The rest of the paper is organized as follows. In Section II, we describe quantum kinetic equation and super-fermion formalism. Section III presents the main equations of nonequilibrium second-order many-body perturbation theory. Section IV describes numerical calculations. Conclusions are given in Section V. We use natural units throughout the paper: $\hbar = k_B = |e| = 1$, where $-|e|$ is the electron charge.

II. LINDBLAD KINETIC EQUATION AND SUPER-FOCK SPACE

To be specific in our discussion, let us consider one spin-degenerate level (impurity) attached to two macroscopic leads. We begin with the Lindblad kinetic equation

$$\begin{aligned} \frac{d\rho(t)}{dt} = & -i[H, \rho(t)] \\ & + \sum_{\sigma k \alpha} \sum_{\mu=1,2} (2L_{\sigma k \alpha \mu} \rho(t) L_{\sigma k \alpha \mu}^\dagger - \{L_{\sigma k \alpha \mu}^\dagger L_{\sigma k \alpha \mu}, \rho(t)\}). \end{aligned} \quad (1)$$

Here H is the *finite* Hamiltonian for the embedded impurity (the "embedded" here means that the systems consists of the impurity itself and finite parts of left/right leads). The Hamiltonian for the embedded impurity can be written in the following form:

$$\begin{aligned} H = & H_S + H_B + H_T, \\ H_S = & \varepsilon_0 \sum_{\sigma} n_{\sigma} + U n_{\uparrow} n_{\downarrow}, \\ H_B = & \sum_{\sigma k \alpha} \varepsilon_{k \alpha} a_{\sigma k \alpha}^\dagger a_{\sigma k \alpha}, \\ H_T = & -t \sum_{\sigma k \alpha} (a_{\sigma k \alpha}^\dagger a_{\sigma} + h.c.), \end{aligned} \quad (2)$$

where a^\dagger, a are fermionic creation and annihilation operators: a_σ^\dagger (a_σ) creates (destroys) an electron with spin σ in the impurity and $a_{\sigma k \alpha}^\dagger$ ($a_{\sigma k \alpha}$) creates (destroys) an electron of energy ε_k and spin $\sigma = \uparrow, \downarrow$ in the left ($\alpha = L$) or right ($\alpha = R$) lead; n_σ is the number operator for electrons of spin σ in the impurity; U is the Coulomb interaction between two electrons of opposite spin in the impurity; t is the tunneling matrix element between the states in the leads and in the impurity. For simplicity we assume that the tunneling matrix element is real and independent of α, k and σ . We also assume that the left and right leads are identical. Here $\sum_{k \alpha}$ runs over $2N$ *discrete* single particle levels $k \alpha$ coupled directly to the Lindblad dissipators.

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The dissipators have the following form:

$$L_{\sigma k \alpha 1} = \sqrt{\Gamma_{k \alpha 1}} a_{\sigma k \alpha}, \quad L_{\sigma k \alpha 2} = \sqrt{\Gamma_{k \alpha 2}} a_{\sigma k \alpha}^\dagger, \quad (3)$$

with $\Gamma_{k \alpha 1} = \gamma_{k \alpha}(1 - f_{k \alpha})$, $\Gamma_{k \alpha 2} = \gamma_{k \alpha}f_{k \alpha}$. Here $f_{k \alpha} = [1 + \exp[(\varepsilon_{k \alpha} - \mu_\alpha)/T_\alpha]]^{-1}$ and $\gamma_{k \alpha}$ is given by the imaginary part of the electrode self energy $\gamma_{k \alpha} = -\frac{1}{2}\text{Im}[\Sigma_{k \alpha}]$.^{8,9} The Lamb shift is included into the single-particle energy of the leads: $\varepsilon_{k \alpha} = \varepsilon_{k \alpha}^{(0)} + \text{Re}[\Sigma_{k \alpha}]$, where $\varepsilon_{k \alpha}^{(0)}$ is bare energy of single-particle levels in the leads.

We would like to emphasize here that for the steady state electron transport calculations the Lindblad master equation can be made as accurate and exact as necessary by the increasing the number of lead states k included into the Hamiltonian for the embedded impurity. So the master equation (1) can be considered as the *exact* starting point for first principles electronic transport calculations.

Let us begin to work with the kinetic equation (1). First, we re-write it in the super-fermion representation. For many-particle quantum systems the density matrix $\rho(t)$ and the Hamiltonian are operators in the Fock space. The Fock space can be defined by some orthonormal complete set of basis vectors:

$$\sum_n |n\rangle\langle n| = I, \quad \langle n|m\rangle = \delta_{nm}. \quad (4)$$

Let us introduce the additional Fock space which is identical copy of the initial Fock space

$$\sum_n |\tilde{n}\rangle\langle\tilde{n}| = \tilde{I}, \quad \langle\tilde{n}|\tilde{m}\rangle = \delta_{nm}. \quad (5)$$

We denote all vectors and operators in this additional Fock space by "tilde". The vectors $|n\rangle$ and $|\tilde{n}\rangle$ span the so-called super-Fock space, which is a direct product of the original and the "tilde" Fock spaces. In the super-Fock space we define "left vacuum vector"

$$|I\rangle = \sum_n \alpha_n |n\rangle \otimes |\tilde{n}\rangle, \quad (6)$$

and "nonequilibrium wavefunction":

$$|\rho(t)\rangle = \rho(t)|I\rangle, \quad (7)$$

where α_n ($|\alpha_n| = 1$) is an arbitrary phase factor. Now the nonequilibrium average can be written as

$$\langle A(t) \rangle = \text{Tr}[A\rho(t)] = \langle I|A|\rho(t) \rangle. \quad (8)$$

We consider a system which consists of fermions distributed over N levels. If we take vector $|n\rangle$ and $|\tilde{n}\rangle$ to be the particle number eigenstate, $|n\rangle = |n_1 n_2 \dots n_N\rangle$, $|\tilde{n}\rangle = |\tilde{n}_1 \tilde{n}_2 \dots \tilde{n}_N\rangle$, and choose $\alpha_n = (-i)^{n_1 + n_2 + \dots + n_N}$, then we can readily demonstrate by the straightforward algebraic manipulations that

$$a_j |I\rangle = -i\tilde{a}_j^\dagger |I\rangle, \quad a_j^\dagger |I\rangle = -i\tilde{a}_j |I\rangle. \quad (9)$$

This is so-called "tilde conjugation rule". It transforms the original operators to the tilde operators and it is one of the most important relations. In particular, it follows from (9) that the left vacuum vector, $|I\rangle$, is always the vacuum for $a_j^\dagger - i\tilde{a}_j$ and $\tilde{a}_j^\dagger + ia_j$ operators. Moreover, it shows that, in some sense, the particle creation (annihilation) in ordinary Fock space is equivalent to the particle annihilation (creation) in the "tilde" space.

We can formulate the following rules for the operations in the super-Fock space:¹⁰⁻¹³

1. The left vacuum vector $|I\rangle$ and the nonequilibrium wavefunction $|\rho(t)\rangle = \rho(t)|I\rangle$ are invariant under the tilde conjugation $|\rho(t)\rangle = |\rho(t)\rangle$, $|\tilde{I}\rangle = |I\rangle$, and $\langle I|\rho(t)\rangle = 1$.
2. Tilde conjugation rules: The main rule is $a_j |I\rangle = -i\tilde{a}_j^\dagger |I\rangle$, $a_j^\dagger |I\rangle = -i\tilde{a}_j |I\rangle$ and as consequence the double tilde conjugation does not change the operator $\tilde{\tilde{A}} = A$ and $(c_1 \tilde{A} + c_2 \tilde{B}) = c_1^* \tilde{A} + c_2^* \tilde{B}$.
3. Evolution of the system is described by the time-dependent Schrödinger equation $i\frac{d}{dt}|\rho(t)\rangle = L|\rho(t)\rangle$, where the Liouvillian is obtained from the corresponding master equation for the density matrix by the tilde conjugation rules. The nonequilibrium average is given by $\langle A(t) \rangle = \langle I|A|\rho(t) \rangle$ and $\langle I|L = 0$.

If we act by the Lindblad equation on the "left vacuum vector" $|I\rangle$, employ the tilde conjugation rules and use the fact that the density matrix $\rho = \rho(a^\dagger, a)$ is the operator in original Fock space therefore it commutes with all "tilde" operators, then the Lindblad master equation becomes the time-dependent Schrödinger equation in the super-Fock space

$$i\frac{d}{dt}|\rho(t)\rangle = L|\rho(t)\rangle \quad (10)$$

where the Liouvillian L is given by

$$L = L_S + L_B + L_T, \quad (11)$$

where $L_S = H_S - \tilde{H}_S$ and $L_T = H_T - \tilde{H}_T$ are both Hermitian, while

$$L_B = H_B - \tilde{H}_B - i \sum_{\sigma k \alpha} \Pi_{\sigma k \alpha} \quad (12)$$

includes the non-Hermitian part which is responsible for the dissipation in the system:

$$\begin{aligned} \Pi_{\sigma k \alpha} = & (\Gamma_{k \alpha 1} - \Gamma_{k \alpha 2})(a_{\sigma k \alpha}^\dagger a_{\sigma k \alpha} + \tilde{a}_{\sigma k \alpha}^\dagger \tilde{a}_{\sigma k \alpha}) \\ & - 2i(\Gamma_{k \alpha 1} \tilde{a}_{\sigma k \alpha} a_{\sigma k \alpha} + \Gamma_{k \alpha 2} \tilde{a}_{\sigma k \alpha}^\dagger a_{\sigma k \alpha}^\dagger) + 2\Gamma_{k \alpha 2}. \end{aligned} \quad (13)$$

In the above equations all tilde operators are obtained from non-tilde ones by the tilde conjugation rules.

In this paper, we focus on nonequilibrium steady state, where the density matrix $|\rho(t)\rangle$ has already reached its asymptotic steady state $|\rho_\infty\rangle$ and does not anymore depend on time. Therefore, the electron transport problem is reduced to the problem of finding the eigenvector with zero eigenvalue of complex, non-Hermitian, finite-dimensional Liouville operator (11) acting in the super-Fock space

$$L|\rho_\infty\rangle = 0. \quad (14)$$

Once the steady state density matrix is found, we can compute the current as

$$J_\alpha = -it \sum_{\sigma k} \langle I | (a_{\sigma k\alpha}^\dagger a_\sigma - a_\sigma^\dagger a_{\sigma k\alpha}) | \rho_\infty \rangle. \quad (15)$$

In the next section, we show how one can find $|\rho_\infty\rangle$ perturbatively beyond nonequilibrium Hartree-Fock approximation.

III. NONEQUILIBRIUM MANY-BODY PERTURBATION THEORY

Before we start to develop many-body perturbation theory, we make the important remark on the notation abuse in this section of the paper: only creation/annihilation operators written with letter a (such as for example $a_{k\alpha}$ and $a_{k\alpha}^\dagger$) are related to each other by the hermitian conjugation; all other creation c^\dagger and annihilation c operators are "canonically conjugated" to each other, i.e., for example, c^\dagger does not mean $(c)^\dagger$ although $\{c, c^\dagger\} = 1$.

Let us first perform the normal ordering of the Liouvillian, and find the nonequilibrium Hartree-Fock density matrix $|\rho_\infty^{(0)}\rangle$ and corresponding nonequilibrium quasiparticles (i.e. quasiparticles, which have the Hartree-Fock density matrix as a vacuum in the super-Fock space).

Using the Wick theorem we rewrite the Liouvillian (11) as

$$L = L^{(0)} + L', \quad (16)$$

where L' is the normal ordered part of the Liouvillian

$$L' = U : (a_\uparrow^\dagger a_\uparrow a_\downarrow^\dagger a_\downarrow - \text{t.c.}) :, \quad (17)$$

and the notation (t.c.) means the tilde conjugation (i.e. $a_\sigma \rightarrow \tilde{a}_\sigma$, etc.). The normal ordering is asymmetric: it is performed with respect to $\langle I |$ from the left and the nonequilibrium Hartree-Fock density matrix $|\rho_\infty^{(0)}\rangle$ from the right.¹³

The mean-field part of L is

$$L^{(0)} = L_S^{(0)} + L_T + L_B, \quad (18)$$

where $L_S^{(0)}$ is a quadratic part of L_S in the Hartree-Fock approximation

$$L_S^{(0)} = \sum_{\sigma} (\varepsilon_0 + U \langle n_{-\sigma} \rangle) (a_{\sigma}^\dagger a_{\sigma} - \tilde{a}_{\sigma}^\dagger \tilde{a}_{\sigma}). \quad (19)$$

The mean-field population $\langle n_{\sigma} \rangle = \langle I | n_{\sigma} | \rho_\infty^{(0)} \rangle$ is spin independent and $\langle a_{\sigma}^\dagger a_{-\sigma} \rangle = 0$ due to the symmetry of the problem. The quadratic part of the Liouvillian, $L^{(0)}$, can be diagonalized exactly in terms of nonequilibrium quasiparticle creation and annihilation operators.¹³ As a result we get

$$L^{(0)} = \sum_{n\sigma} (\Omega_n c_{\sigma n}^\dagger c_{\sigma n} - \Omega_n^* \tilde{c}_{\sigma n}^\dagger \tilde{c}_{\sigma n}), \quad (20)$$

where the nonequilibrium quasiparticles are defined as

$$\begin{aligned} c_{\sigma n}^\dagger &= \psi_n (a_{\sigma}^\dagger - i\tilde{a}_{\sigma}) + \sum_{k\alpha} \psi_{n,k\alpha} (a_{\sigma k\alpha}^\dagger - i\tilde{a}_{k\alpha}), \\ c_{\sigma n} &= \psi_n a_{\sigma} + i\varphi_n (\tilde{a}_{\sigma}^\dagger + i a_{\sigma}) \\ &\quad + \sum_{k\alpha} (\psi_{n,k\alpha} a_{\sigma k\alpha} + i\varphi_{n,k\alpha} (\tilde{a}_{\sigma k\alpha}^\dagger + i a_{k\alpha})), \end{aligned} \quad (21)$$

and $\tilde{c}_{\sigma n}^\dagger, \tilde{c}_{\sigma n}$ are obtained from $c_{\sigma n}^\dagger, c_{\sigma n}$ by the tilde conjugation rules. The operators $c^\dagger, c, \tilde{c}^\dagger, \tilde{c}$ are connected to $a^\dagger, a, \tilde{a}^\dagger, \tilde{a}$ by canonical (but not unitary) transformations. Nonequilibrium quasiparticle creation and annihilation operators obey the fermionic anticommutation relations. By the construction, $\langle I |$ is the left vacuum for $c_n^\dagger, \tilde{c}_n^\dagger$ operators. The vacuum state for c_n, \tilde{c}_n operators, $|\rho_\infty^{(0)}\rangle$, is automatically the zero-eigenvalue eigenstate of the mean-field Liouvillian $L^{(0)}$, and therefore, it is the steady state density matrix in the Hartree-Fock approximation:

$$L^{(0)} |\rho_\infty^{(0)}\rangle = 0, \quad \langle I | \rho_\infty^{(0)} \rangle = 1. \quad (22)$$

In other words, the mean-field density matrix is the density matrix which does not contain nonequilibrium quasiparticle excitations.

The amplitudes $\psi_n, \psi_{n,k\alpha}$ and quasiparticle energies Ω_n ($n = 1, \dots, 2N + 1$) are the solution of the following eigenvalue problem (obtained from the equations-of-motion $[L, c_{\sigma n}^\dagger] = \Omega_n c_{\sigma n}^\dagger$)

$$\begin{aligned} \varepsilon_{HF} \psi_n - t \sum_{k\alpha} \psi_{n,k\alpha} &= \Omega_n \psi_n, \\ E_{k\alpha} \psi_{n,k\alpha} - t \psi_n &= \Omega_n \psi_{n,k\alpha}, \end{aligned} \quad (23)$$

where $E_{k\alpha} = \varepsilon_{k\alpha} - i\gamma_{k\alpha}$ and $\varepsilon_{HF} = \varepsilon_0 + U \langle n_{\sigma} \rangle$ is the Hartree-Fock single particle energy. The amplitudes $\psi_n, \psi_{n,k\alpha}$ are normalized as

$$\psi_n \psi_{n'} + \sum_{k\alpha} \psi_{n,k\alpha} \psi_{n',k\alpha} = \delta_{nn'}. \quad (24)$$

The amplitudes $\varphi_n, \varphi_{n,k\alpha}$ satisfy the following nonhomogeneous system of linear equations (obtained from

$$[L, c_{\sigma n}] = -\Omega_n c_{\sigma n}:$$

$$\begin{aligned} (\varepsilon_{HF} - \Omega_n)\varphi_n - t \sum_{k\alpha} \varphi_{n,k\alpha} &= t \sum_{k\alpha} f_{k\alpha} \psi_{n,k\alpha}, \\ (E_{k\alpha}^* - \Omega_n)\varphi_{n,k\alpha} - t\varphi_n &= -tf_{k\alpha}\psi_n. \end{aligned} \quad (25)$$

This is a set of nonlinear equations since the Hartree-Fock single particle energy ε_{HF} depends on amplitudes

$$\langle n_\sigma \rangle = \sum_n \psi_n \varphi_n, \quad (26)$$

which in turn depends on ε_{HF} . We solve these equations numerically by self-consistent iterations. We first guess the population $\langle n_\sigma \rangle$, then for a given ε_{HF} we solve the eigenvalue problem (23). Then we solve the linear system of equations (25) with the known quasiparticle spectrum Ω_n and known amplitudes $\psi_n, \psi_{n,k\alpha}$. Then we compute new nonequilibrium mean-field population $\langle n_\sigma \rangle$ of the impurity and continue this loop for self-consistent iteration until the variation in the impurity population between the iterations becomes negligible.

Now we are in a position to develop the post-Hartree-Fock many-body perturbation theory, which takes into account the normal ordered part of the Liouvillian (17). We introduce the continuous real parameter λ , which will be set to unity in the end of the calculations

$$L = L^{(0)} + \lambda L'. \quad (27)$$

The normal ordered post-Hartree-Fock perturbation L' in the nonequilibrium quasiparticle basis is given in the Appendix. We expand the exact steady state density matrix in powers of λ ,

$$|\rho_\infty\rangle = |\rho_\infty^{(0)}\rangle + \lambda |\rho_\infty^{(1)}\rangle + \lambda^2 |\rho_\infty^{(2)}\rangle + \dots, \quad (28)$$

where $\langle I | \rho_\infty^{(p)} \rangle = 0$, $p \geq 1$. If we require that $|\rho_\infty\rangle$ is the steady state density matrix for the full Liouvillian (14), we get the following recurrent relations for the p th-order correction to the Hartree-Fock density matrix:

$$L_0 |\rho_\infty^{(p)}\rangle = -L' |\rho_\infty^{(p-1)}\rangle. \quad (29)$$

In the case of the second-order perturbation theory this recurrent relation simply becomes the systems of two equations

$$L_0 |\rho_\infty^{(1)}\rangle = -L' |\rho_\infty^{(0)}\rangle, \quad (30)$$

$$L_0 |\rho_\infty^{(2)}\rangle = -L' |\rho_\infty^{(1)}\rangle. \quad (31)$$

Before solving Eqs.(30, 31) for $|\rho_\infty^{(1)}\rangle$ and $|\rho_\infty^{(2)}\rangle$ let us represent the current (15) in terms of nonequilibrium quasiparticles and understand which configurations in nonequilibrium density matrix give nonzero contribution to the expectation value of the current. Using the transformation inverse to (21), we find

$$\begin{aligned} J_\alpha &= -it \sum_{\sigma k n m} \{ (\psi_{n,k\alpha}^* \varphi_m^* - \psi_n^* \varphi_{m,k\alpha}^*) \langle I | \tilde{c}_{n\sigma} \tilde{c}_{m\sigma}^\dagger | \rho_\infty \rangle \\ &\quad + i(\psi_{n,k\alpha}^* \psi_m - \psi_n^* \psi_{m,k\alpha}) \langle I | \tilde{c}_{n\sigma} c_{m\sigma} | \rho_\infty \rangle \}. \end{aligned} \quad (32)$$

The first term here is fully accounted within the Hartree-Fock approximation

$$J_\alpha^{(0)} = -4t \text{Im} \sum_{kn} \psi_{n,k\alpha} \varphi_n, \quad (33)$$

and does not contribute to the expectation value over the correlated density matrix. The p th-order perturbative theory correction to the HF current comes from the second part of Eq.(32)

$$\begin{aligned} J_\alpha^{(p)} &= 2it \sum_{kmn} (\psi_{n,k\alpha}^* \psi_m - \psi_n^* \psi_{m,k\alpha}) F_{mn}^{(p)} \\ &= -4t \text{Im} \sum_{kmn} \psi_{n,k\alpha}^* \psi_m F_{mn}^{(p)}, \end{aligned} \quad (34)$$

where $F_{mn}^{(p)}$ is the expansion coefficient in

$$|\rho_\infty^{(p)}\rangle = i \sum_{\sigma mn} F_{mn}^{(p)} c_{\sigma m}^\dagger \tilde{c}_{\sigma n}^\dagger |\rho_\infty^{(0)}\rangle + \dots \quad (35)$$

and $F_{mn}^{(p)} = (F_{nm}^{(p)})^*$ as follows from $|\rho_\infty^{(p)}\rangle = \widetilde{|\rho_\infty^{(p)}\rangle}$.

Thus, to find the p th-order correction to the Hartree-Fock current we need to calculate $F_{mn}^{(p)}$. Since L' is normal ordered it does not contain terms quadratic in nonequilibrium quasiparticle creation operators. Therefore, as it can be easily seen from Eq.(30), $F_{mn}^{(1)} = 0$, and the first nonvanishing correction to the current is $J_\alpha^{(2)}$.

Eq.(30) gives the first-order perturbation theory correction to the Hartree-Fock steady state density matrix. It contains the mixture of four nonequilibrium quasiparticle excitations:

$$|\rho_\infty^{(1)}\rangle = \left\{ \sum_{klmn} G_{klmn}^{(1)} c_{\uparrow k}^\dagger c_{\downarrow l}^\dagger \tilde{c}_{\uparrow m}^\dagger \tilde{c}_{\downarrow n}^\dagger \right\} |\rho_\infty^{(0)}\rangle, \quad (36)$$

where

$$G_{klmn}^{(1)} = -\frac{L_{klmn}^{(2)}}{\Omega_k + \Omega_l - \Omega_m^* - \Omega_n^*} \quad (37)$$

and $G_{klmn}^{(1)} = G_{mnkl}^{*(1)}$. Substituting (36) into (31) we obtain

$$|\rho_\infty^{(2)}\rangle = i \sum_{\sigma mn} F_{mn}^{(2)} c_{\sigma m}^\dagger \tilde{c}_{\sigma n}^\dagger |\rho_\infty^{(0)}\rangle + \dots, \quad (38)$$

where

$$F_{mn}^{(2)} = \frac{1}{\Omega_m - \Omega_n^*} \sum_{ijk} \{ L_{mijk}^{(5)} G_{kjni}^{(1)} - L_{nijk}^{*(5)} G_{kjmi}^{*(1)} \}. \quad (39)$$

Inserting (39) into (34) we get the second-order perturbation theory correction to the Hartree-Fock current (33).

The omitted terms in (38) contain four, six, and eight excited nonequilibrium quasiparticles and these configurations do not contribute to the current in the second-order perturbation theory. However, they contribute in higher orders. We also note that each term in $|\rho_\infty^{(p)}\rangle$

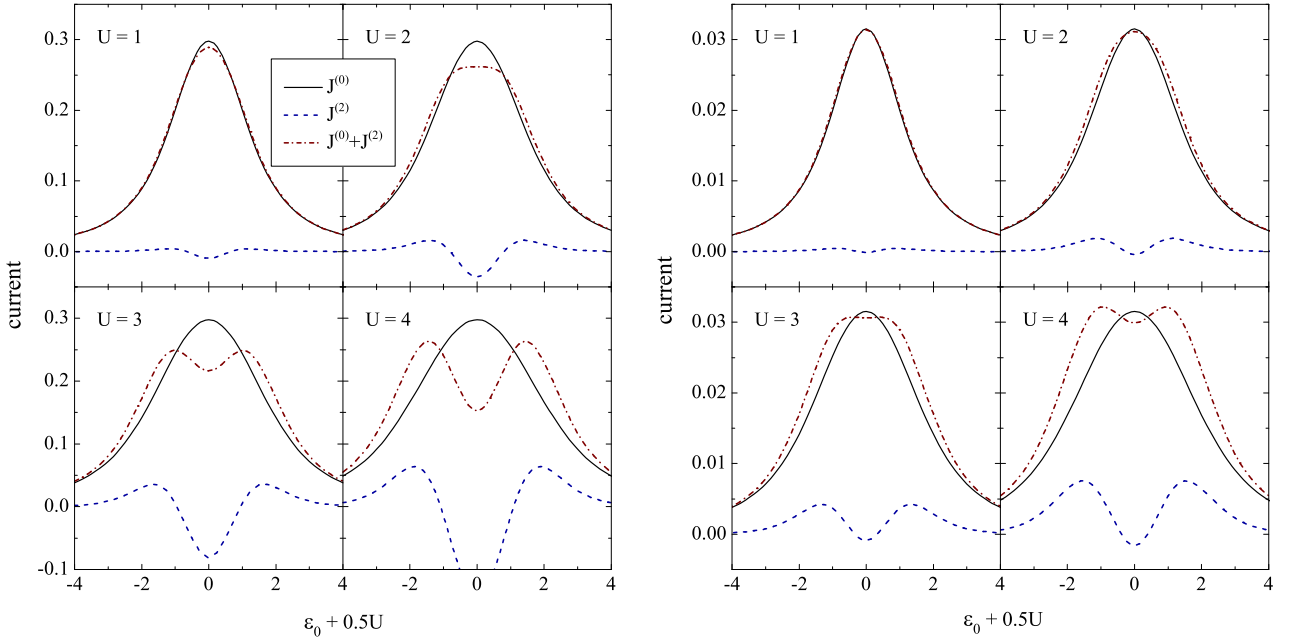


FIG. 1. (Color online): Current in the Anderson impurity model as a function of the central site energy, ε_0 , at applied voltages $V = 1$ (left panels) and 0.1 (right panels) for different values of the Coulomb interaction energy U .

contains even number of excited quasiparticles and the number of tilde and non-tilde creation operators in the excited quasiparticle configurations is the same in all orders of perturbation theory.

To this point, the calculations are valid for arbitrary left and right leads. For the identical leads, Eqs. (33,34) can be further simplified. Indeed, if we have identical left and right leads, i.e., if $E_{kL} = E_{kR} = E_k$, Eq. (23) has N eigenvalues given by $\Omega_n = E_l$. For these eigenvalues $\psi_n = 0$, and $\psi_{n,kL} = -\psi_{n,kR} = -\delta_{kl}2^{-1/2}$. The remaining $N+1$ eigenstates have $\psi_{n,kL} = \psi_{n,kR}$ and hence they do not contribute to the sum over n in Eqs. (33,34). Thus, we obtain

$$J_\alpha^{(0)} = \mp 2^{3/2} t \text{Im} \sum_n \varphi_n, \quad (40)$$

$$J_\alpha^{(p)} = \mp 2^{3/2} t \text{Im} \sum_{mn} \psi_m F_{mn}^{(p)}, \quad (41)$$

where the upper (lower) sign corresponds to $\alpha = L$ (R). In addition, because of $\psi_n = 0$, $L_{nijk}^{(5)} = 0$ and the second term in Eq. (39) vanishes.

Moreover, using explicit expression for φ_n in the case of $\Omega_n = E_l$,

$$\varphi_n = 2^{-1/2} \frac{t(f_{lL} - f_{lR})}{(\varepsilon_{HF} - E_l) + 2t^2 \sum_k \frac{1}{(E_l - E_k^*)}}, \quad (42)$$

we can readily demonstrate that if the macroscopically large part of the leads ($N \rightarrow \infty$, $\gamma_k \rightarrow 0$) is included into the embedded Hamiltonian (2), Eq.(40) becomes the

Landauer formula for the current in the Hartree-Fock approximation (see¹³ for details).

IV. NUMERICAL RESULTS

We perform numerical calculations assuming that each lead has N discrete, spin degenerate energy levels uniformly distributed in the bandwidth $[E_{min} : E_{max}] = [-5 : 5]$. The tunneling coupling strength t is computed from the $\Gamma = 2\pi\eta t^2 = 1$, where $\eta = N/(E_{max} - E_{min})$ is the density of states in the leads. In all our calculations we take $N = 1600$ and $\gamma = 2\Delta\varepsilon$, where $\Delta\varepsilon$ is the energy spacing between states in the leads. Under this choice of the parameters the imaginary part of the self-energy becomes energy independent constant $\Gamma = 1$ within the bandwidth of the leads and vanishes outside the bandwidth. We use a symmetric applied voltage: $\mu_{L,R} = \pm 0.5V$.

To verify that the sufficient number of the leads levels is included into the embedded Hamiltonian (2) we calculated the Hartree-Fock current for two different regimes, for fixed applied voltage V and varying central site energy ε_0 and vice versa, and then compared our results with the Landauer, i.e. exact, mean-field current. We found the disagreement between obtained results is negligible (the maximum deviation $< 1\%$ of the value of the current).

Fig. 1 shows the current plotted as a function of the impurity level for different values of the Coulomb interaction energy U . As we can see the HF current $J_L^{(0)}$ becomes broader with increasing of U and reaches its

maximum value at the symmetric point $\varepsilon_0 = -U/2$. The second order perturbation theory correction to the current is symmetric with respect to $\varepsilon_0 = -U/2$ and can be both positive and negative. We have numerically found that $J_L^{(2)} < 0$ only when the Hartree-Fock level ε_{HF} is between μ_L and μ_R . For $U \lesssim 1$ the second order perturbation theory correction to the current is very small, that means the Hartree-Fock approximation accounts for the main part of the electronic interactions. For larger U the second order perturbative corrections change the behavior of the current both qualitatively and quantitatively. For example, when $U = 3$ and $V = 1$ the electronic correlations produce the dip in the current in the vicinity of the symmetric point $\varepsilon_0 = -U/2$.

We found that the larger the voltage (i.e. the further away we are from the equilibrium), the more important role the nonequilibrium electronic correlations play. This is evident from the comparison of the left (computed at $V = 1$) and right (computed at $V = 0.1$) panels of Fig. 1. It means that the nonequilibrium dynamics and electronic correlations are entangled in nontrivial way and the nonequilibrium enhances and amplifies the role of electronic correlations.

V. CONCLUSIONS

In this paper, we developed the second-order post-Hartree-Fock perturbation theory for the electron current through a region of out of equilibrium, interacting electrons. As an example, we considered electron transport through out of equilibrium Anderson model, although all our derivations are also directly applied to a general molecular junctions described by full many-electron Hamiltonian. We started with the Lindblad kinetic equation for the embedded molecular system. We converted the kinetic equation to super-fermion representation and define nonequilibrium quasiparticles within Hartree-Fock approximation. Then we applied the Wick theorem and perform the normal ordering of the Liouvillian with respect to the vacuum for nonequilibrium quasiparticles. We developed the second-order post-Hartree-Fock perturbation theory by admixing two- and four-quasiparticle configurations to the nonequilibrium vacuum. Our numerical calculations for out of equilibrium Anderson impurity demonstrated that nonequilibrium electronic correlations may produce significant quantitative and qualitative corrections to Hartree-Fock electronic transport properties. We also found that the nonequilibrium enhances the role of electronic correlations.

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Appendix A: Normal ordered Liouvillian in the basis of nonequilibrium Hartree-Fock quasiparticles

Here we give the explicit expression of L' in terms of nonequilibrium quasiparticle creation and annihilation operators. Using the inverse transformation

$$\begin{aligned} a_\sigma^\dagger &= \sum_n (\psi_n - \varphi_n) c_{\sigma n}^\dagger + i \sum_n \psi_n^* \tilde{c}_{\sigma n}, \\ a_\sigma &= \sum_n \psi_n c_{\sigma n} - i \sum_n \varphi_n^* \tilde{c}_{\sigma n}^\dagger \end{aligned} \quad (A1)$$

we obtain

$$\begin{aligned} L' = U : (a_\uparrow^\dagger a_\uparrow a_\downarrow^\dagger a_\downarrow - \text{t.c.}) : \\ = \sum_{klmn} \left\{ (L_{klmn}^{(1)} c_{k\uparrow}^\dagger c_{l\downarrow}^\dagger c_{m\downarrow} c_{n\uparrow} - \text{t.c.}) \right. \\ + L_{klmn}^{(2)} c_{k\uparrow}^\dagger c_{l\downarrow}^\dagger \tilde{c}_{m\uparrow}^\dagger \tilde{c}_{n\downarrow}^\dagger \\ + L_{klmn}^{(3)} (c_{k\uparrow}^\dagger c_{l\downarrow}^\dagger \tilde{c}_{m\downarrow} c_{n\uparrow} + c_{k\downarrow}^\dagger c_{l\uparrow}^\dagger \tilde{c}_{m\uparrow} c_{n\downarrow} \\ - c_{k\uparrow}^\dagger \tilde{c}_{l\uparrow}^\dagger \tilde{c}_{m\downarrow} c_{n\downarrow} - c_{k\downarrow}^\dagger \tilde{c}_{l\downarrow}^\dagger \tilde{c}_{m\uparrow} c_{n\uparrow}) \\ + i [L_{klmn}^{(4)} (c_{k\uparrow}^\dagger c_{l\downarrow}^\dagger \tilde{c}_{m\downarrow} c_{n\uparrow} + c_{k\downarrow}^\dagger c_{l\uparrow}^\dagger \tilde{c}_{m\uparrow} c_{n\downarrow}) + \text{t.c.}] \\ \left. + i [(L_{klmn}^{(5)} c_{k\uparrow}^\dagger \tilde{c}_{l\downarrow} c_{m\downarrow} c_{n\uparrow} + c_{k\downarrow}^\dagger \tilde{c}_{l\uparrow} c_{m\uparrow} c_{n\downarrow}) + \text{t.c.}] \right\}, \end{aligned} \quad (A2)$$

where $L_{klmn}^{(i)}$ are given by

$$\begin{aligned} L_{klmn}^{(1)} &= U(\psi_k \psi_l - \psi_k \varphi_l - \varphi_k \psi_l) \psi_m \psi_n, \\ L_{klmn}^{(2)} &= U[(\psi_k - \varphi_k)(\psi_l - \varphi_l) \varphi_m^* \varphi_n^* \\ &\quad - \varphi_k \varphi_l (\psi_m^* - \varphi_m^*)(\psi_n^* - \varphi_n^*)], \\ L_{klmn}^{(3)} &= U(\varphi_k \psi_l^* - \psi_k \varphi_l^*) \psi_m^* \psi_n, \\ L_{klmn}^{(4)} &= -U[(\psi_k - \varphi_k)(\psi_l - \varphi_l) \varphi_m^* \\ &\quad + \varphi_k \varphi_l (\psi_m^* - \varphi_m^*)] \psi_n, \\ L_{klmn}^{(5)} &= U\psi_k \psi_l^* \psi_m \psi_n. \end{aligned}$$

It is notable that because of $\langle I | L = 0$, L' does not contain terms of four annihilation operators.

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